U.S. DEPARTMENT OF COMMERCE
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PB80-142201

Great Smoky Mountain Preliminar Study for Biosphere Reserve Pollutant Monitoring

(U.S.) Environmental Monitoring Systems Lab, Las Vegas

Nov 79

TECHNICAL REPORT DATA
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1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-79-072		PB 80 142201

4. TITLE AND SUBTITLE	5. REPORT DATE
GREAT SMOKY MOUNTAINS PRELIMINARY STUDY FOR BIOSPHERE RESERVE POLLUTANT MONITORING	November 1979
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) G. B. Wiersma, R. W. Brown, R. Hermann, C. Taylor and J. Pope	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Monitoring Systems Laboratory Office of Research and Development U.S. Environmental Protection Agency Las Vegas, NV 89114	10. PROGRAM ELEMENT NO. XH1627J
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency-Las Vegas, NV Office of Research and Development Environmental Monitoring Systems Laboratory Las Vegas, NV 89114	13. TYPE OF REPORT AND PERIOD COVERED Final
	14. SPONSORING AGENCY CODE EPA/600/07

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A presampling of physical and biological media at preselected locations on the Great Smoky Mountains Biosphere Reserve was completed. The media collected, which included air, water, soils, litter, and various plant species, were used to determine elemental concentrations and to help in the design of an efficient and cost-effective monitoring system.

The results showed that air concentrations of trace elements were below detectable limits. Indications of organic air contaminants were evident.

A number of compounds such as zinc, toluene, and methylene chloride were found in water. In addition, dimethyl hexene, ethyl benzene, and phthalate esters are suspected water contaminants.

Analytical results of the vegetation, soils, and litter showed a variety of elemental contamination. The concentration of lead in the litter layer at four sampling sites ranged from 246 to 469 ppm. These data, similar to those reported by other researchers showed that lead levels increased with altitude.

Based upon a field sampling error of plus or minus 10 percent at the 95 percent confidence level, the number of samples required to satisfy this condition, based upon the samples/element combination, was calculated.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
environmental biology site survey pollution	Biosphere Reserves Great Smoky Mountains soils plants water air	06F 08G 08H

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	
	20. SECURITY CLASS (This page)	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

*U.S. GOVERNMENT PRINTING OFFICE: 1979— 683-282/2211

United States
Environmental Protection
Agency

Environmental Monitoring
Systems Laboratory
P.O. Box 15027
Las Vegas NV 89114

EPA-600/4-79-072
November 1979

PB80-142201

Research and Development

EPA

Great Smoky Mountain Preliminary Study for Biosphere Reserve Pollutant Monitoring

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EPA-600/4-79-072
November 1979

GREAT SMOKY MOUNTAINS PRELIMINARY STUDY FOR BIOSPHERE RESERVE POLLUTANT MONITORING

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FOREWORD

Protection of the environment requires effective regulatory actions based on sound technical and scientific information. This information must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of exposure to specific pollutants in the environment requires a total systems approach that transcends the media of air, water, and land. The Environmental Monitoring Systems Laboratory-Las Vegas contributes to the formation and enhancement of a sound monitoring data base for exposure assessment through programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment
- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs

This report presents the results of the field sampling program carried out in the fall of 1977. This was a multi-media, integrated sampling effort. Data collected gave estimates of detection limits, variability and levels of certain pollutants. Problems of logistics and access were dealt with. This study provides a basis for an expanded sampling program in the Great Smoky Mountain Biosphere Reserve which will help achieve the ultimate goal to develop a responsive and cost effective pollutant monitoring system for biosphere reserves in general.

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Director
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SUMMARY

A preliminary sampling program was initiated in the Great Smoky Mountains National Park, Tennessee, and North Carolina. This national park of 209,000 hectares was selected to be a part of the Southern Appalachian Biosphere Reserve cluster. It serves as a permanent reservoir of genetic material and a site where natural ecosystems can be sampled, studied, and preserved.

An interest in the state of the environment as indicated in the framework of the Man and Biosphere Program (MAB) necessitates the assaying and documentating of the environmental quality in these preserves. For this reason, a monitoring program was initiated. This initial program, a mutual effort by the U.S. Environmental Protection Agency and the U.S. National Park Service, had two objectives. The first objective was to determine the levels of trace elements and organic contaminants in physical and biological media. The second objective, following data analysis and evaluation, was to design an effective and cost-efficient pollutant monitoring system.

Physical and biological media sampled included air, water, soils, litter, and various plant species. Analytical results of these samples showed a variety of elemental contamination. The concentration of lead in litter at four sampling sites was of particular importance. The concentration ranged from 246 to 469 parts per million. These data, similar to those reported by other researchers, showed that lead levels increase with altitude.

A field sampling error of plus or minus 10 percent at the 95 percent confidence level was desired. The number of samples required to satisfy this condition for a permanent monitoring system, based upon the sample/element combination, was determined and used in subsequent studies.

Environmental monitoring, as defined by the U.S. Environmental Protection Agency, is the systematic collection of physical, chemical, biological, and related data pertaining to environmental quality, pollution sources, and other factors that influence or are influenced by environmental quality. Environmental quality data are essential for determining the exposure of critical populations at risk. Such data are obtained by establishing monitoring systems to identify and measure pollutants and their concentrations in air, water, vegetation, soil, and food. The identification and measurement of pollutants in preserved areas, such as the biosphere reserves, may permit the monitoring of subtle deleterious processes that may be masked in areas of high impact. In identifying and measuring the exposure of receptor communities to chemical or physical agents, monitoring data provide the basis for quantitating the contributions of environmental pathways for each chemical or physical form of the pollutant.

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INTRODUCTION

Man's impact on the environment is far-reaching and at times catastrophic. Gone are the days when the pollution emitted by man was assumed to impact only his immediate surroundings. Today, pollution problems are recognized as truly global in nature; they transcend geographic and political boundaries.

Elgmork et al. (1973) reported that snow in Norway contained several pollutants. They found levels of lead in the snow up to 98 micrograms per liter (µg/l), sulphur levels of 8.5 milligrams per liter (mg/l), and pH values as low as 3.25. The remoteness of these sampling areas from Norway's limited automobile and industrial areas precluded pollutant deposition from local sources. The researchers concluded that these pollutant levels resulted from contaminated air masses being brought in by low-pressure systems from the great industrial and urban areas of western and central Europe. Another study by Johnson et al. (1972) showed that streams in New England were acidified primarily through the washout of sulphur compounds during local rains. Most of this sulphur originated from the combustion of fossil fuels from large industrial centers of the eastern and central United States. Schlesinger et al. (1974) also reported that lead, cadmium, and mercury were present in precipitation on Mount Moosilauke in New Hampshire. They determined that low pressure-system tracks in North America coming from the large population and industrial areas of the central and mid-Atlantic regions of the United States converged on the northern New England States.

Lazarus et al. (1970) reported that increased levels of lead, zinc, copper, iron, nickel, and manganese were found in rainwater collected by a nationwide precipitation network. They concluded that man's industrial activities were the primary source of these pollutants in the rainwater. The highest overall concentrations occurred in the northeastern portion of the United States. Also, a significant statistical correlation existed between the lead concentrations at each precipitation sampling station and the quantity of gasoline sold in the vicinity of each of the collection points.

Chow and Earl (1970), studying lead aerosols in the vicinity of San Diego, California, reported that only a small fraction of the lead aerosols are deposited near the source of emission. They hypothesized that the majority of lead particulates are transported by major air currents and deposited throughout the world. Hirao and Patterson (1974) studied lead levels in Thompson Canyon, a remote site on the High Sierra Crest. According to their data, the 14-square-kilometer (km) watershed received 16 kilograms

(kg) of deposited lead per year. It was further determined that 97 percent of this lead was from anthropogenic sources. They stated:

> "These findings show that a widespread assumption, that lead pollution is mainly confined to urban complexes and is essentially absent in open country, is improbable. . . ."

In addition to lead, other elements have been shown to be transported on a global basis. Weiss et al. (1971) sampled the Greenland icecap and presented data showing mercury levels that indicated a possible buildup of mercury in the ice sheet. For example, in samples representing deposition prior to 1952, the mean mercury concentration was 60 ± 17 nanograms per kilogram (ng/kg) of water. Samples representing deposition from 1952 to 1965 had a mean concentration of 125 ± 52 ng/kg of water.

Zoller et al. (1974) analyzed atmospheric particulate material at the South Pole for 22 elements. Antimony, lead, selenium, and bromine were all highly enriched over what could be expected from earth crustal values. They postulated that the source of these compounds was from high-temperature combustion of volcanic activity or from manmade fossil-fuel burning.

Global transport has also been confirmed for other pollutants such as DDT. For example, Anas and Wilson (1970) reported that northern fur seals collected on the Pribilof Islands, Alaska, in 1969 contained DDT and its isomers in both the nursing pup's fat tissue and in the mother's milk.

Concern over the widespread global contamination from man's activities has been one of the driving forces behind the attempt to establish a global network of biosphere reserve sites. The Study of Critical Environmental Problems Report (Massachusetts Institute of Technology, 1970) stated:

> "Over the past few years, the concept of the earth as a 'spaceship' has provided many people with an awareness of the finite resources and the complex natural relationships on which man depends for his survival. These realizations have been accompanied by concerns about the impacts that man's activities are having on the global environment. Some concerned individuals, including well-known scientists have warned of both imminent and potential global environmental catastrophes."

A variety of organizations and committees--including the International Task Force of the Global Network for Environmental Monitoring; the Global Monitoring Task Force of SCOPE (Scientific Committee on Problems of the Environment); the Man and Biosphere Expert Panel on Pollution; the Study of Critical Environmental Problems (SCEP); Task Force II, Committee on International Environmental Affairs; and the SCOPE Commission on Environmental Monitoring Assessment--have called for the formation of a global monitoring network.

The United Nations Conference on the Human Environment (Man and Biosphere, 1974) held in Stockholm in June 1972 recommended the establishment

of the United Nations Environment Program. It also recommended the establishment of EARTHWATCH, which has a four-pronged program including monitoring, research, evaluation, and information exchange. The ultimate objective of EARTHWATCH was the establishment of a Global Environmental Monitoring System (GEMS). As part of this Global Environmental Monitoring System, it was recommended that biosphere reserves be established. The UN Conference on the Human Environment in 1972 also recomemnded that biological reserves be established within the framework of the Man and Biosphere Program. In addition, a report entitled "Man's Impact on the Global Environment," published by the Massachusetts Institute of Technology in 1970, recommended similar entities, calling them ecological baseline stations in remote areas or biosphere reserves.

Biosphere reserves may be defined as undisturbed and protected natural background areas of the Earth where life processes occur with minimal human interference. The requirements for, and the value of, biosphere reserves have previously been described in the report of the Ad Hoc Task Force on GNEM (Global Network for Environmental Monitoring) (1970) and the SCOPE Report No. 3 (Munn, 1973).

Specifically, the biosphere reserves were established to:

1. provide a permanent record of the state of the environment;

2. ensure the availability of undisturbed areas from which background data on pollutant levels could be obtained;

3. give indication of increasing levels of global pollution; and

4. serve as repositories for natural sources of genetic pools of animal and plant species.

Franklin (1976, 1977) identified the research and monitoring activities for which the reserves could be used. These included:

1. long-term baseline studies of environmental and biologic features;

2. research to help develop management policies for the reserves;

3. experimental or manipulative research;

4. environmental monitoring; and

5. study sites for selected MAB research projects.

A detailed concept paper has been published on the general approach to a pollutant monitoring system for biosphere reserves (Wiersma et al., 1978). In addition results from preliminary studies on the Great Smoky Mountains were presented at the Fourth Joint Conference on Sensing of Environmental Pollutants (Wiersma et al., 1977).

This report is the compilation and analysis of data generated from a monitoring study conducted in the Great Smoky Mountains National Park in cooperation with the U.S. Environmental Protection Agency (EPA) and the U.S. National Park Service. The objectives were to determine minimum pollutant levels, to identify the variability of collected samples, and to evaluate sampling techniques. Media sampled included air, water, unincorporated litter, soils, and vegetation.

CONCLUSIONS

The results and techniques identified indicate that sampling problems such as logistics and access into relatively remote areas are not limiting factors in the establishment of a pollutant monitoring system. Analytical detection limits employing techniques as described in this report for vegetation, soils, and litter were adequate for the completion of the stated objectives. Detection limits for selected trace elements in air will have to be improved either by analytical techniques or in sampling equipment design. Field sampling error, which was relatively high, can be adjusted by sampling design.

The collection of physical and biological data from natural areas within the Great Smoky Mountains National Park will establish the necessary criteria to develop a comprehensive pollutant monitoring program. Sampling techniques used, combined with long-term monitoring data, will serve to identify baseline conditions, identify pollutant concentrations, determine trends, and define physical and biological responses to man-induced contaminants.

FIELD SAMPLING METHODS

SOIL AND VEGETATION SAMPLING AND SITE DESCRIPTION

Four sampling sites within the national park were chosen for investigation. Vegetation, water, and unincorporated litter, defined as organic debris and its underlying fermentation layer, were collected at each site. Two of the sites were located on the north slope of the Great Smoky Mountains, a third on top of a ridge, and the fourth on the south-facing side of the park. The site locations are shown on Figure 1, labeled as 11, 12, 13, and 14.

Site 11 was located on the north side of the park at an elevation of about 1,100 m; this site was in a mature hardwood/hemlock forest. Species common in the overstory included hemlock, sugar maple, black cherry, tulip poplar, and magnolia. The understory was made up primarily of rhododendron.

Nine sampling points were originally planned per site using a 3 x 3 grid system. The distance between each grid point was to be 200 m. However, the thick understory and steep slopes at site 11 prevented this sampling scheme. The nine sampling points were laid out along a trail at 200-m intervals. Each sampling point was 40 m up slope from the trail.

Unincorporated litter was sampled at 10 locations evenly spaced around a 10-m diameter circle at each of the 9 sampling points at site 11. A 1-liter sample was collected at each location around the circle. The ten 1-liter samples were placed in a clean plastic bag and thoroughly mixed. After mixing, a 0.5-liter aliquot was collected and placed in a polyethylene container. At each of these 10 locations, a 5-centimeter (cm) deep soil sample was collected after the unincorporated litter layer was removed. In a manner similar to the unincorporated litter mixing and sampling techniques, the 10 soil samples were placed in a clean plastic bag, thoroughly mixed, and then subsampled. At each of the 10 sample points, 2 species of plants were sampled. The plant tissues collected were new leaf growth. For site 11, a 1-liter water sample was collected from a tributary stream near Roaring Fork Creek. Table 1 shows the kinds and number of samples collected at each site.

Sampling site 12 was located on Porters Flat at an elevation of 800 m. This site was composed primarily of 40-year-old second-growth hardwood. Hardwoods common in the overstory included hemlock, sugar maple, tulip poplar, and beech. The method of sampling was identical to that used at site 11. A 1-liter water sample was also collected at the footbridge on Porters Creek. A summary of the samples collected is presented in Table 1.

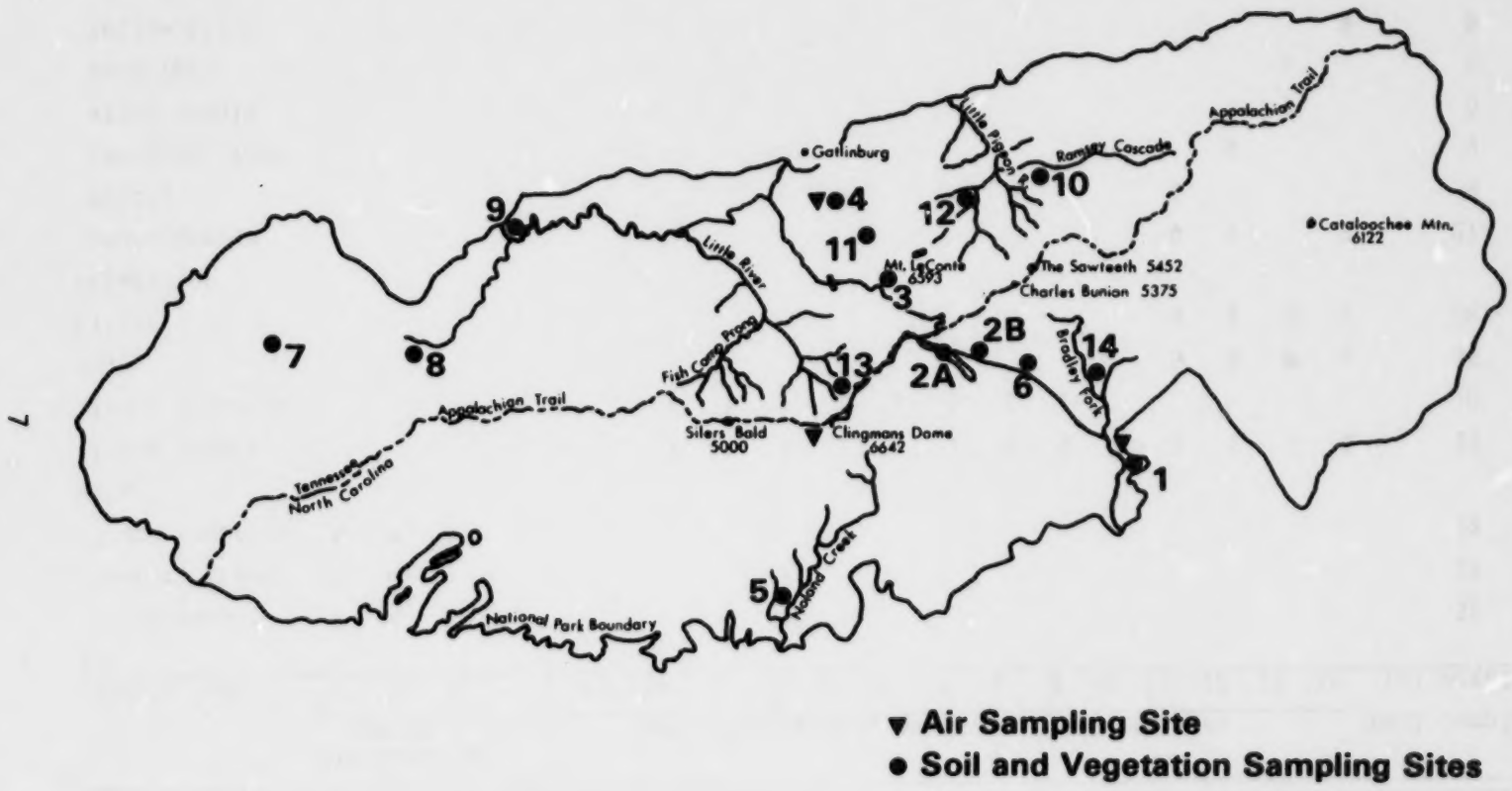

Figure 1. Sampling site locations in the Great Smoky Mountains National Park.

TABLE 1. SUMMARY OF TYPES AND NUMBERS OF SAMPLES COLLECTED AT THE GREAT SMOKY MOUNTAINS NATIONAL PARK

	Air Sampling Sites			Soil, Vegetation, and Water Sampling Sites															Total Samples
Sample Type	1	2	3	1	2A	2B	3	4	5	6	7	8	9	10	11	12	13	14	Collected
Air																			
Trace metals	4	4	4																12
Mercury traps	4	4	4																12
Trace organics	4	4	4																12
Water																			
Trace metals				1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	15
Trace organics				1		1	1	1	1	1	1	1	1						10
Soil															9	9	9	9	36
Litter															9	9	9	9	36
Vegetation																			
Rhododendron															9	9		9	27
Nettle															9				9
Christmas fern																9			9
Witch hobble																	9		9
Wood fern																	9		9
Yellow birch																		9	9

Sampling site 13 was located on Mount Collins, about 3.3 km east of Clingmans Dome at an elevation of 1,800 meters (m). The topography at this site was relatively flat. The understory vegetation was dense, composed primarily of witch hobble, while the overstory was made up of mature red spruce and Fraser fir. A 3 x 3 grid design with 200 m between sampling points was used. A 1-liter water sample was collected from a spring 50 m below the site. Samples collected at this site are shown in Table 1.

Sampling site 14, located on the south side of the park, was 2.5 km north of the trail head at Smokemount Campground. The elevation at this site was 800 m. Sampling was conducted along Bradley Fork. The techniques used were identical to those used at sites 11 and 12. The water sample was collected from a tributary stream of Bradley Fork. The vegetation on this site was second-growth hardwood, about 40 years old and similar in composition to vegetation at site 12.

WATER SAMPLING

In addition to the four 1-liter water samples collected at sites 11, 12, 13, and 14, a variety of streams draining both the north and south slopes of the park were sampled. These sites, chosen with the aid of park personnel, were representative of the area's main drainage systems.

At each of these sampling sites a 1-liter sample was collected. The sample was placed in a Teflon bottle and immediately acidified with nitric acid. In addition, a 19.2-liter glass carboy was filled with water. The glass carboy had been previously cleaned to remove possible contamination by trace organics. Each of the 1-liter samples was analyzed for trace elements. The carboy samples collected for trace organic analyses were composited with the entire amount extracted.

The water sampling sites identified below are also shown on Figure 1.

1 - Oconaluftee River, at the bridge on Tow String Road
2A - Beechflat Creek, above the road cut on Highway 441 (trace element sample only)
2B - Beechflat Creek, directly below the road cut on Highway 441
3 - Walker Prong, 30 m east of Highway 441
4 - Twin Creeks, approximately 60 m from the Uplands Field Research Station
5 - Nolan Creek, about 1.7 km north of Fontana Lake Highway
6 - Beechflat Creek, 1.7 km below the cut on the east side of Highway 441
7 - Abrams Creek, near Cades Cove
8 - Abrams Creek, about 0.4 km east of the Cades Cove area
9 - Little River, about 90 m below the confluence of the Little River and the Middle Prong of the Little River
10 - Ramsey Cascade Creek, about 2.5 km from the bridge

AIR SAMPLES

Air samples were collected at three sites in the park (see Figure 1). One site was located at the Uplands Field Research Station near Gatlinburg, Tennessee (air site 3). A second (air site 2) was located at Clingmans Dome, the highest point in the park. The third was located at the Wranglers Corral near the intersection of Tow String Road and the Oconaluftee River on the south side of the park (air site 1).

At each station, three air samples were collected. One was analyzed for mercury, the second for trace elements, and the third for trace organics.

The mercury collection system, previously identified by Long et al. (1973), was composed of a 20-cm long, 5-millimeter (mm) diameter glass tube filled with silver wool. Air was pumped through the glass tube-silver wool trap at a flow rate of approximately 50 milliliters per minute (ml/min). After sampling, the trap was sealed, transported to the laboratory, and analyzed by a direct current plasma emission analytical system.

The second type of air monitoring device, for trace elements, consisted of a 0.8-micrometer (μm), type AA Millipore filter. After collection, the Millipore membrane filters were analyzed by photon-induced X-ray fluorescence as described by Jaklevic et al. (1976), Jaklevic et al. (1973), and Dzubay and Stevens (1975).

The third type of air sampler was a TEMPEST high-volume instrument utilizing a Bureau of Mines 3B-06 charcoal cartridge and a Whatman prefilter. Sampling was conducted at a flow rate of 13 cubic meters per hour (m^3/h). The charcoal cartridge and the prefilter were sent to the University of Iowa and analyzed for organic compounds by standard extraction and gas chromatograph techniques.

ANALYTICAL TECHNIQUES AND RESULTS

WATER

Organic Analyses

Analysis of Purgeable Volatile Organics--

The Environmental Protection Agency's Surveillance and Analysis Division of Region IV in Athens, Georgia, analyzed this group of samples by the purge-and-trap method. The results of these analyses using a gas chromatograph-mass spectrometer (GC-MS) detection system with a minimum detectable limit of 0.5 mg/liter showed that only methylene chloride, chloroform, acetone, n-hexane, and isoctane were found in the samples. However, the concentrations of these compounds were less than the calibration blanks: therefore, no purgeable organic compounds will be reported as being present in the biosphere samples.

Analysis of Non-Purgeable Volatile Organics--

Eight 19.2-liter wide-mouth bottles were washed with detergent and then rinsed three separate times with tapwater, distilled water, and acetone. After drying in an oven, each bottle was rinsed with a separate solution of 100 ml of methylene chloride. The washings were combined and then evaporated to 1 ml with a Kuderna-Danish (K-D) evaporator and micro-K-D. The washings were analyzed for impurities by gas chromatography using a 6-m x 2-mm i.d. glass column packed with 1 percent SP-2250 on 100/120 Supelcoport. The carrier gas used was 27 to 29 ml/min of helium. The injector temperature was 275°C and the FID detector temperature was 300°C. The temperature program called for 4 min at 50°C, rising 8°C/min to 260°C, with a final hold of 20 min. The injection size was 2 ml, and the attenuation was set so that 40 ng injected gave 10 to 90 percent deflection. The washings did not show any contaminants.

After the mouths were sealed with aluminum foil, the sample bottles were transported to the Great Smoky Mountains. As previously mentioned, the samples were collected throughout the national park (see Figure 1 for exact locations). One of the samples was lost during shipment because of container breakage.

The resins chosen for the accumulator columns were XAD-8, XAD-4/8, and 35/60 mesh Tenax. The XAD-4/8 is an equal dry-weight mixture of XAD-4 and XAD-8. All had been precleaned and stored for several months under methanol. About 50 ml of each resin were placed in separate chromatography tubes and washed with solvent. The XAD resins were washed with acetone and methylene chloride, and the Tenax was washed with acetone. The last 100-ml portion of effluent was collected, evaporated, and gas chromatographed as previously

described. Solvent impurities were also checked by gas chromatography. If peaks were present in the chromatograms, the washing process was repeated until either the chromatograms were free of peaks or the peaks had been reduced to an insignificant level.

The resins were placed in three separate columns connected in series. After the sample had passed through, they were stripped of accumulated organics and examined separately. The first column was XAD-8 because it was believed to reversibly sorb humic acids. It also served as a protector column for the XAD-4/8 column, protecting the XAD-4 resin from contamination by irreversibly sorbed humic material. The third column, Tenax, was used mainly to accumulate other compounds passing through the two previous columns.

This sampling train met the requirements of the project but was not ideal. Water passed from the sample bottle through a 60-mm i.d. Teflon tube to a glass connector on top of the first column. It went through the column, out a U-tube, up through the second column, through an inverted U-tube, and down through the third column. The water was forced through the train by a peristaltic pump attached to the bottom of the third column. A number of problems occurred with this system. First, a planned flow rate of 100 ml/min could not be maintained. Also, because of the short lengths of resin packing relative to the entire length of the column, several void areas within the system occurred. In addition, the columns would not hold the desired 50 ml of resin.

Because of these problems, the final dimensions and configuration of the accumulator columns were 14.6 ml of XAD-8 in a 13-cm x 1.2-cm i.d. column (ratio of length to diameter of 10.8), 26.6 ml of XAD-4/8 in a 13.3-cm x 1.6-cm column (length: diameter 8.3), and 45.5 ml of Tenax in a 14.5-cm x 2.0-cm column (length: diameter 7.2). The flow rate averaged about 40 ml/min.

The analytical techniques were designed to detect organics in water at 0.1 parts per billion (ppb). To test the analytical system, decadeutero anthracene and 1,2-diphenyl hydrazine were selected as internal standards. Both of these compounds as well as azobenzene, a degradation product of 1,2-diphenyl hydrazine, are unlikely to be found in water.

Two separate standards were prepared for each of these two compounds in methylene chloride. One hundred microliters (µl) of each solution was then dissolved in a liter of water. The liter of standard solution contained 16 µg of the deuterated anthracene and 200 µg of 1,2-diphenyl hydrazine, which represented approximately 0.1 ppb and 1.0 ppb concentrations, respectively. The first set was extracted with methylene chloride, concentrated, and gas chromatographed as described previously for the sample-bottle washings. The hydrazine (azobenzene) peak was about 60 percent of full scale while the deuterated anthracene was only about 4 percent of full scale as shown in Figure 2. The experiment did indicate that a detection limit of 0.1 ppb would be attainable.

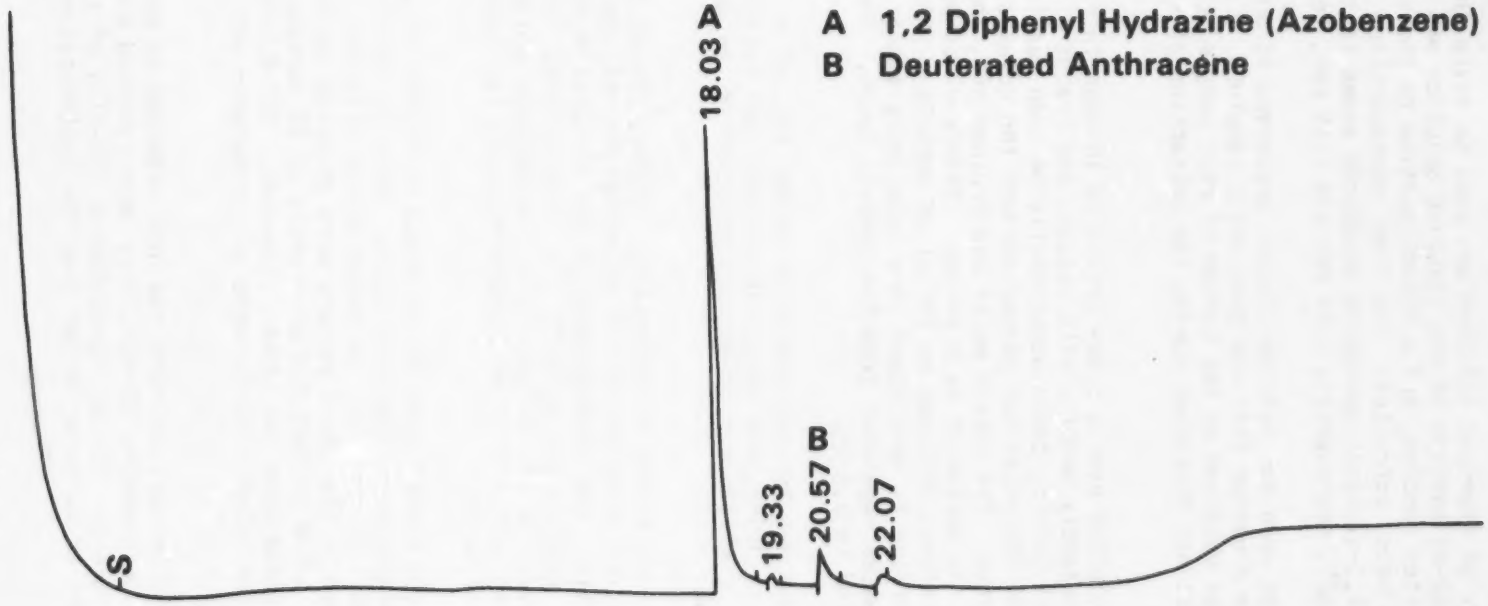

Figure 2. Gas chromatogram (FID) of internal standards, deuterated anthracene, and 1,2-diphenyl hydrazine.

The second liter of standard solution was used to spike the collected water samples. A 100-ml portion of the standard solution was added to each of the seven 19.2-liter samples, and a 200-ml portion to the eighth and ninth sample as they were being extracted. The final concentration of the anthracene and the 1,2-diphenyl hydrazine standards added to the water samples was 0.094 µg/l, representing 0.09 ppb and 1.19 ppb, respectively.

The water samples were not refrigerated or preserved in any way, and they remained sealed with aluminum foil and tape until sampled. A slight deposit of black sediment was observed on the bottom of each sampled container. This deposit, however, was not disturbed during the extraction of water from the bottles.

Sampling was conducted over a 5-day period in 16-hour increments. The sample train was constantly under a mild vacuum, and traces of air, probably from the ground-glass joints, could occasionally be seen passing through the system. After all of the water had passed through the columns, they were removed from the system. The excess water was drained off, and a stopcock adapter attached to the bottom of each column. Thirty ml of acetone was then added to the XAD-8 column, followed by 120 ml of methylene chloride. The combined collected effluents were mixed in a separatory funnel, with the small top layer of water separated from the organic layer. The organic extract was evaporated to 0.5 ml.

The XAD-4/8 column was treated similarly except that 50 ml of acetone and 200 ml of methylene chloride were used. The extract was evaporated to 0.87 ml. A small amount of white precipitate was observed in the extract following evaporation.

The Tenax column was eluted in two stages. First, 100 ml of acetone was added. It was dewatered by adding 200 ml of methylene chloride. After removing the water layer, the organic portion was evaporated to 10 ml. An additional 250 ml of acetone was added to the Tenax column. After collecting, it was added to the orignal 10 ml concentrate and evaporated to 1 ml. In addition, solvent blanks were prepared using the same amounts of solvents plus 10 ml of water.

The samples and the blanks were all examined by GC/FID using the GC conditions and procedures described previously. Most of the eluted compounds were found in the XAD-8 (Figure 3). No peaks having different retention times from those found in the XAD-8 extract were observed in the XAD-4/8 and Tenax extracts. The XAD-8 extract had nine peaks of 10 percent or more of full scale. Two of these were the spiked standards. XAD-4/8 had four peaks, and Tenax had two. The solvent blanks were all acceptable with essentially no discernible peaks.

After the three individual extracts had been examined by gas chromatography-mass spectrometry (GC-MS), they were combined and concentrated to 0.4 ml with a micro-K-D. The gas chromatogram (GC-FID) of this extract showed only four peaks as large or larger than the deuterated anthracene standard (Figure 4).

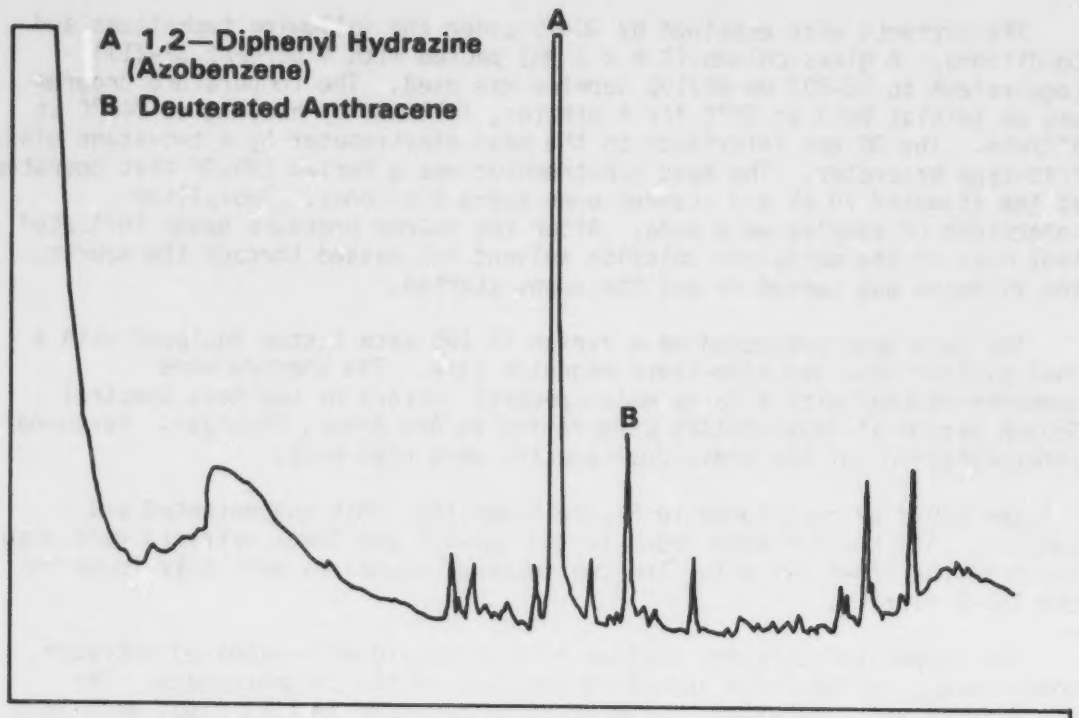

Figure 3. Gas chromatogram (FID) of biosphere reserve XAD-8 extract.

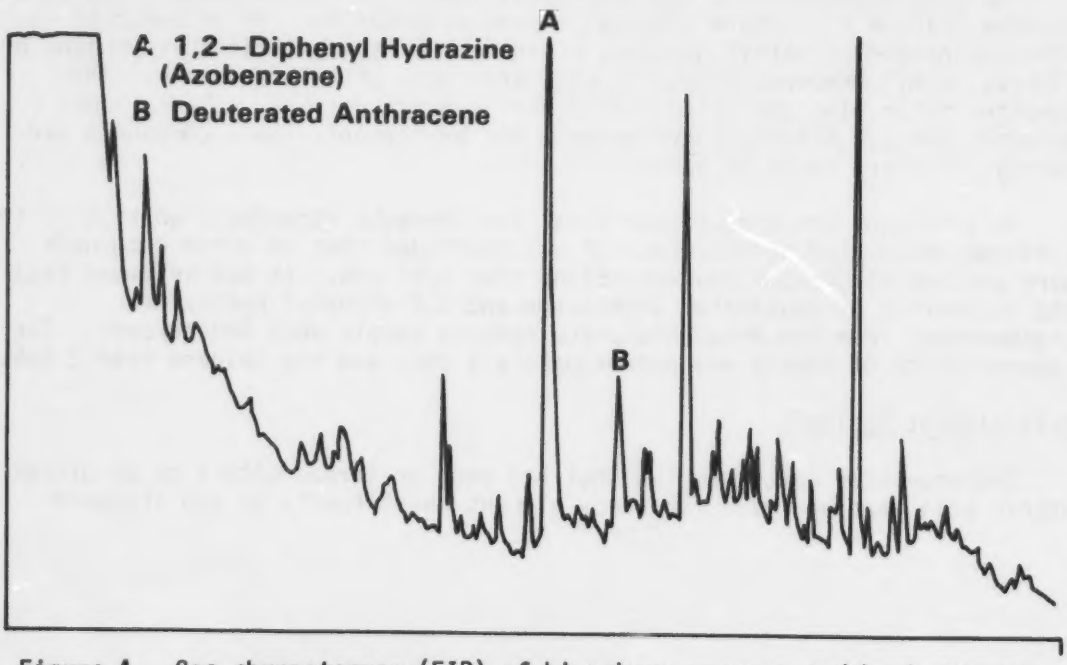

Figure 4. Gas chromatogram (FID) of biosphere reserve combined extracts.

The extracts were examined by GC-MS under the following techniques and conditions. A glass column (3 m x 3 mm) packed with 4 percent SP-2100 (equivalent to SE-30) on 80/100 Supelco was used. The temperature program was an initial hold at 50°C for 4 minutes, followed by heating to 240°C at 8°C/min. The GC was interfaced to the mass spectrometer by a two-stage glass frit-type separator. The mass spectrometer was a Varian CH5-DF that operated at the standard 70 eV and scanned once every 5 seconds. Two-µliter injections of samples were made. After the source pressure gauge indicated that most of the methylene chloride solvent had passed through the source, the filament was turned on and the scans started.

The data were processed on a Varian SS 166 data system equipped with a dual platter disc and nine-track magnetic tape. The spectra were computer-matched with a large mass spectral library by the Mass Spectral Search System at Cyphernetics Corporation in Ann Arbor, Michigan. Personnel interpretations of the individual spectra were also made.

The XAD-8 extract shown in Figure 5 was the most concentrated and complex. All contaminants found in the XAD-4/8 and Tenax extracts were also found in the XAD-8 extract. The two internal standards were only found in the XAD-8 extract.

The composited extract, similar to the individually examined extracts, showed peaks in the first and third portions of the chromatograms. The sensitivity and resolution of the GC-MS system used in this study were less than the FID gas chromatograph.

The only compound that was definitely identified in the water samples was toluene (Figure 6). There also was strong evidence for the presence of dimethyl hexene or methyl heptene, nonane or an isomer, trimethyl benzene or isomers, ethyl benzene, ethyl toluene, and three phthalate esters. The computer match also indicated that 2,4-di-t-butyl anisole, 2,5-di-t-amyl quinone, and 1,2,4-tri-t-butyl anisole may be present; these compounds are rarely, if ever, found in water.

Only toluene and nonane gave total ion currents stronger than that of the 0.09-ppb deuterated anthracene. It was concluded that no other compounds were present at greater concentrations than 0.09 ppb. It was believed that the recoveries of deuterated anthracene and 1,2-diphenyl hydrazine (azobenzene) from the dosed biosphere reserve sample were 100 percent. The concentration of nonane was approximately 1 ppb, and the toluene near 2 ppb.

Multielement Analysis

The one-liter water samples that had been preserved with 1 ml of ultrex nitric acid were analyzed for trace element constituents by two standard

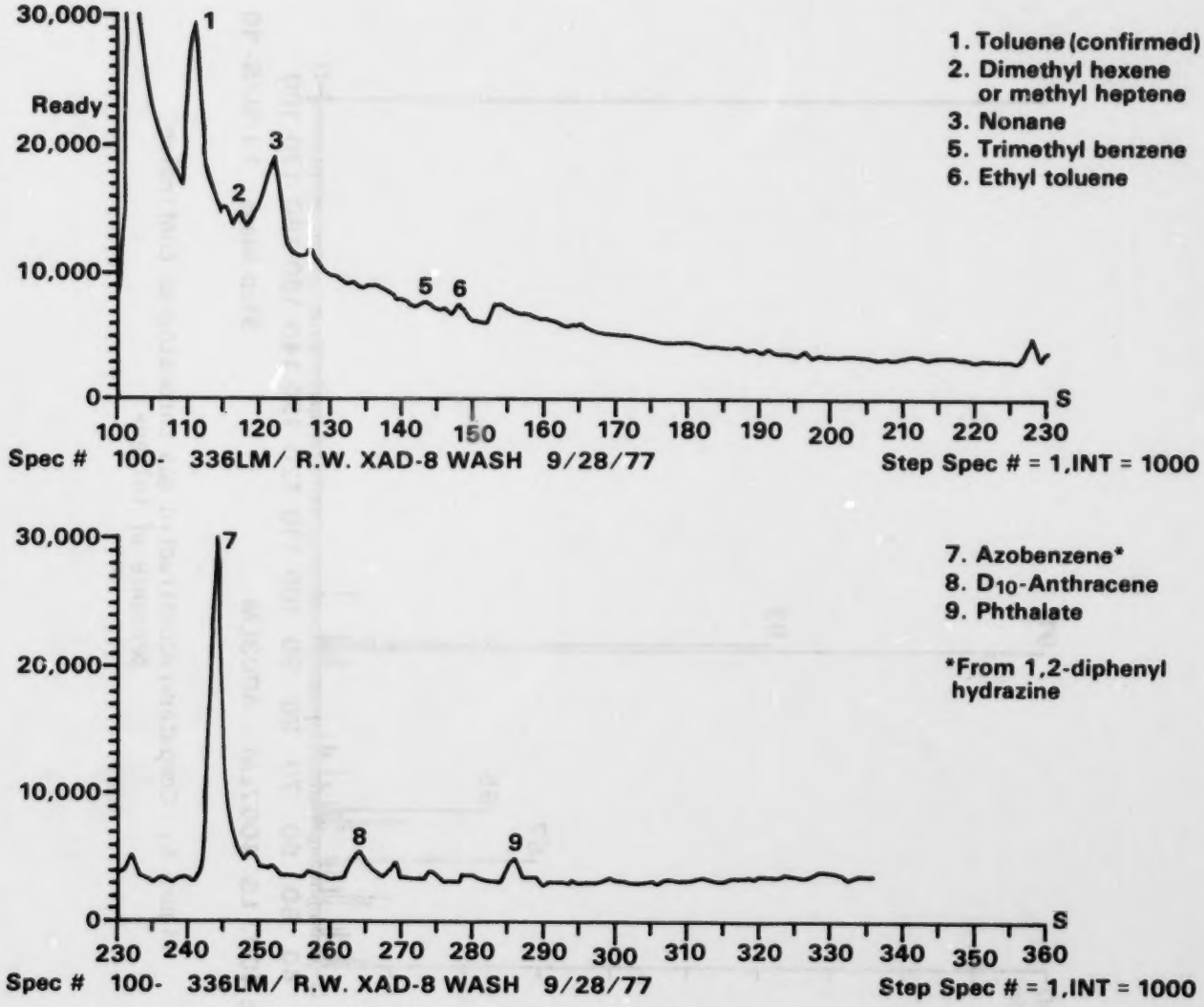

Figure 5. Computer-reconstructed gas chromatogram of biosphere reserve XAD-8 extract.

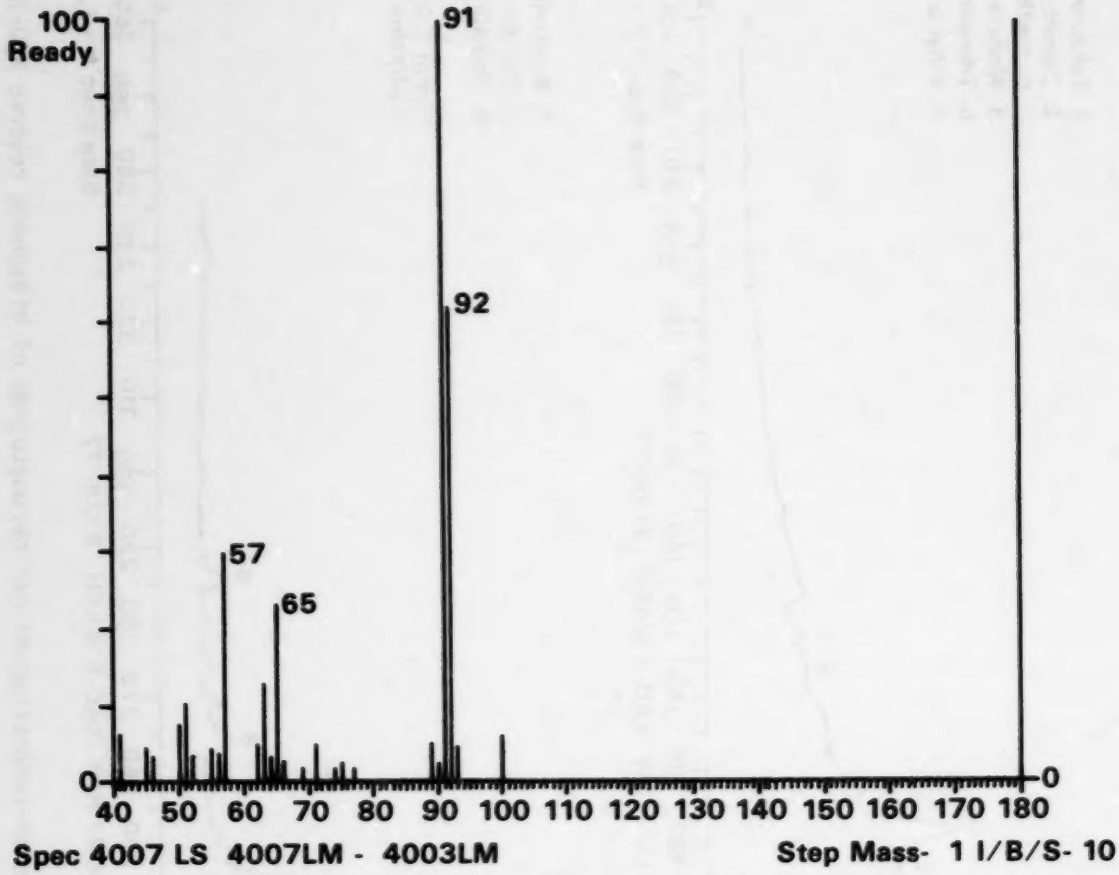

Figure 6. Computer-reconstructed gas chromatogram confirming presence of toluene.

multielement techniques--inductively coupled plasma emission spectrometry (ICPES), and spark source mass spectrometry (SSMS). The ICPES was used because it is capable of giving rapid and accurate determinations of a specific group of 26 elements. The SSMS was used to provide a survey analysis of the entire spectrum of elements, except for the gases.

The procedures and techniques used for the multielement analysis have been previously described by Elgmork et al. (1973) and Johnson et al. (1972).

The results, which are summarized in Tables 2 and 3, show the the concentration range, average concentration, and frequency of occurrence for each element. Two samples, one from site 2B and the other from site 7, were not in the data shown in Tables 2 and 3. The reason for their omission was that the water from site 2B was collected below a construction area and the water from site 7 was collected at a point just below a cattle-grazing area.

Table 4 summarizes the results of all elements analyzed jointly by ICPES and SSMS analyses. The limit of detection for the SSMS for all elements was 0.001 mg/liter. The detection limits of ICPES are indicated by less than values shown on Table 4. The samples for SSMS were prepared in glass containers and were possibly contaminated with boron and silicon. For this reason, no analyses for these elements were reported.

As shown on Table 4, these samples all contained very low levels of most elements. Of the consent-decree elements, only zinc was found.

The zinc in the water sample collected at site 6 is of special interest because it was collected from an area that occasionally displays a white deposit on the stream rocks. U.S. National Park Service personnel suspected this deposit to be an aluminum salt; however, the aluminum concentration, 0.078 µg/liter, is below the average concentration shown on Table 2. This sample was also higher than the average in manganese content.

AIR

The results from the Millipore filters indicated no detectable levels of trace elements. Based on the maximum flow rates used and the detection limits, a "less than" level can be determined. For lead (Pb) it was estimated that, using a filter with 10.75-cm^2 area with a detection limit of 70 ng Pb/cm^2 of filter area and a maximum air volume sampled of 14.6 m^3, the minimum detectable limit would be approximately 50 ng of Pb/m^3 of air. It is not unreasonalbe to expect that the air concentration of lead in the park would be low. Jaklevic et al. (1976) reported that lead levels in air collected from rural areas contained approximately 100 ng/m^3. Chow and Earl (1970) reported an average lead concentration in air of 50 ng/m^3 at Mount Laguna, 45 miles from San Diego. An increase in flow rate or sampling time would increase the sensitivity of this system. The air sampling system employed has, with modification, been used successfully in remote areas of the Great Smoky Mountains National Park. This system has been described by Brown et al. (1979).

TABLE 2. SUMMARY OF ANALYSES OF ELEMENTS DETERMINED BY ICPES AND SSMS (mg/liter)

Element	Range	Average	Frequency (in 13) samples
Ag	ND*	<0.001†	0
Al	(0.380-0.030)	0.111	13
As	ND	<0.001	0
B	(0.007-0.005)	0.0054	5
Ba	(0.020-0.005)	0.010	13
Be	ND	0.001	0
Ca	(13.5-0.53)	2.09	13
Cd	ND	<0.001	2
Co	(0.003-<0.001)	0.001	7
Cr	(0.005-<0.001)	0.001	7
Cu	(0.007-<0.001)	0.002	9
Fe	(0.17-0.05)	0.036	12
Hg	ND	<0.010	0

Element	Range	Average	Frequency (in 13 samples)
Mg	(1.19-0.12)	0.32	13
Mn	(0.12-0.002)	0.021	13
Mo	(0.001-<0.001)	<0.001	2
Ni	(0.001-<0.001)	<0.001	3
Pb	ND	<0.001	0
Sb	ND	<0.001	0
Se	ND	<0.001	0
Sn	ND	<0.001	0
Sr	(0.054-0.006)	0.014	13
Ti	(0.004-<0.001)	0.002	6
V	ND	<0.001	1
Y	ND	<0.002	0
Zn	0.014	0.014	1

* ND signifies the element was Not Detected in any sample
† Values shown as "less than" (<) are detection limits

TABLE 3. SUMMARY OF ANALYSES OF ELEMENTS DETERMINED BY SSMS ONLY (mg/liter)

Element	Range	Average	Frequency (in 13 samples)
Ce	0.001-<0.001	<0.001	1
Rb	0.003-0.001	0.002	13
Br	0.04-<0.001	0.010	12
Ga	0.05-<0.001	0.001	10
Sc	0.002-<0.001	0.001	6
K	0.9-0.1	0.38	13
S	2-0.1	0.48	13
P	0.02-0.003	0.011	13
Na	6-0.2	1.2	13
F	0.01-0.001	0.003	12

The mercury air traps and the associated analytical methods used indicated that mercury levels were not above background.

The charcoal filters were operated for the purpose of detecting organics in air. Only two of the charcoal cartridges were analyzed for organics. These samples included:

I.D. No.	Location	Operating Time (hrs)	Volume
3C-3	Uplands Field Research Station (Gatlinburg, Tennessee)	24	314 m^3
1C-4	Ocanaluftee River (Cherokee, North Carolina)	9.9	125.2 m^3

The samples were prepared and analyzed as follows. The charcoal was removed from the metal canisters, placed in a flask, and shaken vigorously with 100 ml of petroleum ether. The sample was filtered with the petroleum ether concentrated by nitrogen blown down to 5 ml. The granules were then placed in another flask and shaken vigorously with carbon disulfide. Again the sample was filtered and the extract concentrated to 5 ml. The samples were then analyzed by gas chromatography using a 63-Ni detector.

The results are shown in Table 5 and in Figures 7 and 8 for the petroleum ether extraction only. Compound identifications were not performed, but the

TABLE 4. RESULTS OF MULTIELEMENT ANALYSES USING ICPES AND SSMS FOR GREAT SMOKY MOUNTAINS WATER SAMPLES (mg/liter)

	Sample Number													
	1		2A		2B		3		4		5		6	
Element	ICPES	SSMS	ICPES	SSMS	ICPES	SSMS	ICPES	SSMS	ICPES	SSMS	ICPES	SSMS	ICPES	SSMS
Silver	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001
Aluminum	.043	.03	.053	.040	1.77	1.0	.18	.4	.042	.04	.030	.07	.078	.04
Arsenic	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001
Boron	<.005	*	.007	*	.012	*	.005	*	<.005	*	<.005	*	<.005	*
Barium	.005	.004	.008	.004	.016	.007	.006	.002	.013	.02	.006	.002	.016	.01
Beryllium	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001
Calcium	.93	.5	1.77	2.5	3.76	2.5	.92	1.2	1.36	1.0	.56	.2	2.85	2.0
Cadmium	<005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001
Cobalt	<.005	.001	<.005	.003	<.005	.008	<.005	<.001	<.005	<.001	<.005	<.001	<.005	.002
Chromium	<.005	<.003	<.005	.001	<.005	.001	<.005	<.001	<.005	.005	<.005	<.001	<.005	.001
Copper	<.005	.001	<.005	.001	<.005	.004	<.005	.001	<.005	<.001	<.005	.004	<.005	<.001
Iron	.014	.01	.009	.02	.018	.02	.034	.02	.005	<.001	.02	.01	.005	.005
Mercury	.01	**	.01	**	.01	**	.01	**	.01	**	<.01	**	<.01	**
Magnesium	.2	.2	.34	.3	1.5	1.0	.25	.2	.23	.2	.12	.2	.84	1.0
Manganese	.002	.006	.003	.003	1.36	2.0	.038	.05	.004	.002	.003	.009	.12	.1
Molybdenum	<.01	<.001	<.01	<.001	.014	.007	<.01	.009	<.01	<.001	<.01	<.001	<.01	.001
Nickel	<.005	.001	<.005	<.001	.018	.03	<.005	<.001	<.005	.001	<.005	<.001	<.005	<.001
Lead	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001
Antimony	<.010	<.001	<.010	<.001	<.010	<.001	<.010	<.001	<.010	<.001	<.010	<.001	<.010	<.001
Selenium	<.05	<.001	<.050	<.001	<.05	.003	<.050	<.001	<.050	<.001	<.050	<.001	<.050	<.001
Tin	<.05	<.001	<.050	<.001	<.05	<.001	<.050	<.001	<.050	<.001	<.050	<.001	<.050	<.001
Strontium	.008	.004	.018	.02	.025	.03	.006	.005	.012	.008	.006	.003	.024	.02
Titanium	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	.003	<.005	.002	<.005	.004
Vanadium	<.005	.001	<.005	<.001	<.005	.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001
Ytterbium	<.002	***	<.002	***	.011	***	<.002	***	<.002	***	<.002	***	<.002	***
Zinc	<.005	.001	<.005	.001	.075	.04	<.005	<.001	<.005	<.001	<.005	<.001	.014	.005

(continued)

* Samples prepared in glass
** Not reported by SSMS
*** Internal standard

TABLE 4. (Continued)

Element	Sample Number 7 ICPES	7 SSMS	8 ICPES	8 SSMS	9 ICPES	9 SSMS	10 ICPES	10 SSMS	11 ICPES	11 SSMS	12 ICPES	12 SSMS	13 ICPES	13 SSMS	14 ICPES	14 SSMS
Silver	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001
Aluminum	.13	.2	.052	.08	.05	.09	.072	.04	.044	.04	.046	.08	.38	.3	.3	.3
Arsenic	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001
Boron	.005	*	<.005	*	.005	*	<.005	*	<.005	*	<.005	*	<.005	*	<.005	*
Barium	.014	.01	.007	.005	.007	.007	.010	.01	.01	.02	.006	.002	.002	.008	.02	.05
Beryllium	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001	<.002	<.001
Calcium	13.5	17.0	.80	.60	1.15	1.0	.94	.5	1.07	1.0	.82	.7	.53	.4	.72	.5
Cadmium	<.005	<.001	<.005	.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001
Cobalt	<.005	.003	<.005	<.001	<.005	<.001	<.005	.002	<.005	<.001	<.005	.001	<.005	.003	<.005	<.001
Chromium	<.005	.003	<.005	.003	<.005	<.001	<.005	.002	<.005	<.001	<.005	.002	<.005	<.001	<.005	<.001
Copper	<.005	.005	<.005	<.001	<.005	.004	<.005	.007	<.005	.001	<.005	.002	<.005	.004	<.005	<.001
Iron	.11	.3	.023	.03	.025	.02	.008	.01	.031	.07	.005	.002	.005	.001	.17	.1
Mercury	<.010	**	<.010	**	<.01	**	<.010	**	<.01	**	<.01	**	<.01	**	<.01	**
Magnesium	1.19	1.0	.14	.4	.22	.5	.18	.3	.16	.3	.22	.5	.15	.1	.15	.3
Manganese	.015	.02	.006	.01	.003	.007	.003	.002	.002	.002	.002	.002	.031	.05	.05	.05
Molybdenum	<.010	<.001	<.010	<.001	<.01	<.001	<.010	<.001	<.01	<.001	<.01	<.001	<.01	<.001	<.01	<.001
Nickel	<.005	.001	<.005	<.001	<.005	.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001
Lead	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001
Antimony	<.01	<.001	<.01	<.001	<.01	<.001	<.01	<.001	<.01	<.001	<.01	<.001	<.01	<.001	<.01	<.001
Selenium	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001
Tin	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001	<.05	<.001
Strontium	.054	.09	.008	.007	.009	.003	.008	.01	.01	.008	.006	.009	.005	.002	.01	.02
Titanium	<.005	.001	<.005	<.001	<.005	.004	<.005	.002	<.005	<.001	<.005	.002	<.005	<.001	<.005	<.001
Vanadium	<.005	.004	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001
Ytterbium	<.002	***	<.002	***	<.002	***	<.002	***	<.002	***	<.002	***	<.002	***	<.002	***
Zinc	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001	<.005	<.001

* Samples prepared in glass
** Not reported by SSMS
*** Internal standard

TABLE 5. SUMMARY OF RETENTION VOLUMES (cc) FOR ^{63}Ni GAS CHROMATOGRAPHIC ANALYSES OF CHARCOAL FILTER SAMPLES NO. 1C-4 AND 3C-3 (Petroleum Ether Extracts)

Instrument Parameters	Peak No.	Retention Volume (cc) 3C-3 (North Side)	1C-4 (South Side)
Column temperature = 55°C	1	---	30
Detector temperature = 272°C	2	---	40
	3	50	50
	4	70	---
	5	100	---
	6	110	---
	7	---	120
	8	150	150
	9	160	---
	10	300	---
	11	370	370
Column temperature = 104°C	1	---	10
Detector temperature = 273°C	2	20	20
	3	30	30
	4	40	40
	5	50	---
	6	---	60
	7	120	120
	8	160	---
	9	220	---
	10	---	230
Column temperature = 151°C	1	10	10
Detector temperature = 273°C	2	20	20
	3	40	40
	4	60	60
	5	110	---
	6	---	150
	7	160	---
Column temperature = 190°C	1	---	6
Detector temperature = 276°C	2	20	20
	3	30	30
	4	70	70
	5	---	100
	6	---	130
	7	---	150
	8	---	210
	9	---	320

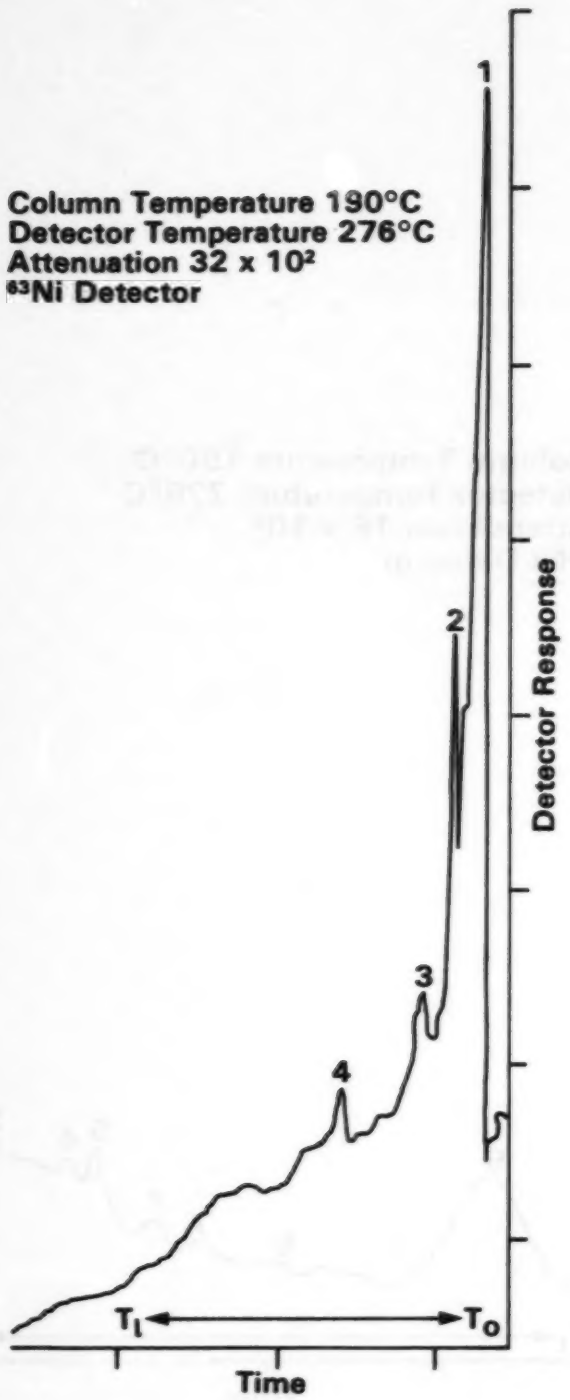

Figure 7. Chromatogram of petroleum ether extract of sample 3C-3.

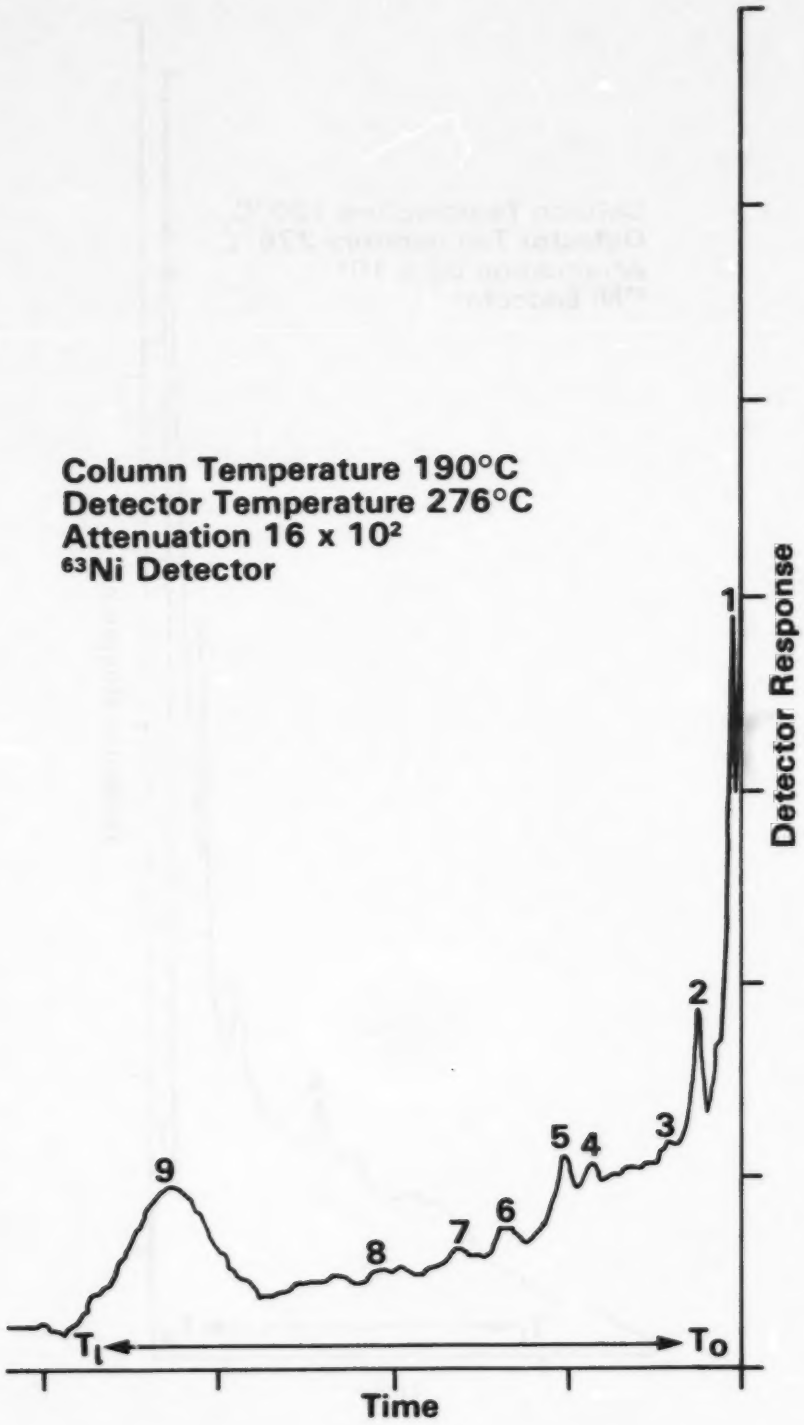

Figure 8. Chromatogram of petroleum ether extract of sample 1C-4.

comparisons of peaks between samples taken from the two sides of the park are of particular interest as shown in Table 5. All samples had a 2-µl injection volume, chart speed was 2 min/cm, and carrier gas flow was 50 ml/min.

No attempt was made to identify the individual peaks. It is assumed most of the organics detected are of natural origin. Considerably more research and developmental effort is required before identification of airborne anthropogenic organics in background areas such as the Great Smoky Mountains can be accomplished.

In summary, the compounds detected at each site have either identical retention volumes or very similar retention volumes. Large differences in retention volumes occurred only when the column temperature was raised to 190°C.

VEGETATION AND LITTER

The vegetation was analyzed by the University of California's (UCLA) Laboratory of Nuclear Medicine and Radiation Biology. This analytical technique has been previously described by Alexander et al. (1975).

Vegetative standards obtained from the U.S. Bureau of Standards with certified trace element levels were submitted as quality assurance samples. Based upon the results of these standards, expected precision limits were calculated for this analytical technique. The precision limits are presented as follows:

Elements	Maximum Allowable % Deviation From a Known Value or COV of Replicates
K, Ca, Mg, Cu, Mn, B, Sr, Ba, Al	±20%
P, Na, Zn, Fe, Cr, Ag, Ti, V	±40%
Li, Pb	±50%

Minimum detection limits are:

Element	ppm	Element	ppm	Element	ppm
P	50.0	B	0.2	Sr	0.2
Na	1.0	Al	0.1	Ba	0.2
K	150.0	Si	1.0	Li	0.3
Ca	1.0	Ti	0.5	Ag	0.1
Mg	50.0	V	1.0	Sn	0.3
Zn	5.0	Co	1.5	Pb	1.0
Cu	0.2	Ni	0.5	Be	0.2
Fe	0.6	Mo	0.2	Cd	3.0
Mn	0.1	Cr	0.2		

These limits and precision values were accepted by the investigators.

The data for trace element values in vegetation and forest litter by site are summarized in Tables 6 through 17. The purpose in sampling vegetation was to obtain an estimate of field sampling error and to begin to define the possible use of certain types of vegetation for biological monitors.

Estimates of field sample error can be used to determine the number of samples required to reach a certain level of confidence. With the amount of data presented in Tables 6 through 17, it was not feasible to make this calculation for each sample type/element combination. The coeffients of variation are shown in Table 18 for certain elements found in vegetation. With the exception of manganese and aluminum most of the coefficients of variation range between 10 and 30 percent.

Arbitrarily, a desired sampling error of plus or minus 10 percent at the 95 percent confidence level was chosen. For example, if witch hobble, shown in Table 18 above, were chosen as a sample species and strontium as the element, it would be necessary to collect approximately 23 samples. Similar estimates can be made for all species and elements. During field sampling and analysis, the number of samples used would probably be controlled by the sample/element combination with the greatest variability tempered by the resources available.

For samples that exhibit a large coefficient of variation such as the manganese in rhododendron, the number of samples required to meet precision levels as stated would be approximately 100. A decrease in precision of only 2 percent would reduce the number of samples required to 71. Our conclusion concerning the required number of vegetation samples for a biosphere reserve monitoring system is that the number required for our desired confidence level is reasonable, and a cost-effective system can be designed.

Another consideration in determining the number of samples collected is the interaction of analytical error with field sampling error. All vegetation and litter samples in this study were analyzed in triplicate and replicated nine times on each sample site. With this type of design, analysis of variance techniques to determine the variability from the analytical error versus that from field sampling was accomplished (Snedecor, and Cochran 1967). The estimated variance of the sample mean per determination is given by the mean square between blocks (i.e., sites 11, 12, 13, and 14) divided by the total number of determinations. This in turn can be partitioned into the various components that contribute to this variance of the individual sample mean per determination. For example, for cobalt in forest litter, 2.2 percent of the variation per determination is due to analytical error, 11.1 percent is due to subsamples from within each site, and 86.7 percent is due to variation between the sites. For lead in forest litter, the estimated variance of the sample mean per determination is broken into the following relative contributions: 1.9 percent from analytical error, 7.4 percent from variability within a block, and 90.7 percent from variability between sites. In spite of the fact that the precision limits of acceptance for lead are plus or minus 50 percent, this is an example that, as large as the analytical error may be, the field error is much greater. Therefore, to reduce field study error and to increase the reliability of estimating trace element levels, more effort should be expended on collecting

TABLE 6. SUMMARY OF TRACE ELEMENT VALUES IN FOREST LITTER FROM SITE 11

Element	Concentration of Trace Element (ppm) in Subsamples*									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	5883	9587	8773	16433	8800	4857	9167	5590	4263	8150
Barium	188	309	196	208	325	140	281	168	181	222
Beryllium	0.6	0.6	0.5	1.2	0.4	<0.2	0.8	<0.2	0.5	0.5
Boron	32.2	14.6	17.0	13.5	9.6	13.3	11.5	10.2	10.1	14.6
Cadmium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Calcium	680	1419	172	72	304	513	420	1290	1507	708
Chromiumm	14.9	35.4	11.1	27.7	18.2	5.1	15.3	7.7	5.6	15.6
Cobalt	1.5	2.1	1.0	2.6	1.5	1.5	1.5	1.9	1.5	1.7
Copper	18.4	38.8	25.6	40.1	25.2	24.7	23.5	24.7	26.1	27.1
Iron	5560	6653	7043	11367	6633	5893	7000	6123	5427	6855
Lead	217	191	279	314	266	181	323	212	231	246
Lithium	2.0	5.3	4.7	11.6	2.5	1.4	4.1	1.9	1.9	3.9
Magnesium	1397	2970	2190	5290	1787	1303	1987	1160	927	2119
Manganese	320	2220	1095	850	286	227	326	340	320	664
Molybdenum	1.4	2.7	2.2	5.1	2.2	0.8	2.3	1.1	0.9	2.1
Nickel	16.7	31.2	12.3	25.8	17.8	9.4	16.4	12.6	9.1	16.8
Phosphorus	1877	3323	1370	<50	853	<50	1910	<50	<50	1037
Potassium (%)	0.52	2.27	3.05	7.70	1.29	0.06	1.73	0.14	0.09	1.87
Silicon (%)	6.0	8.1	10.0**	8.9	9.5	4.3	6.6	4.6	4.5	7.0
Silver	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sodium	1290	2330	2050	3330	746	150	646	186	150	1210
Strontium	31.6	40.7	17.3	15.9	44.0	29.5	35.4	40.6	49.8	33.8
Tin	<0.3	0.3	<0.3	0.4	1.3	<0.3	0.8	0.6	0.5	0.4
Titanium	786	1590	1707	2373	1513	508	1463	666	465	1230
Vanadium	11.4	17.3	17.9	27.6	16.7	5.9	15.6	8.0	6.0	14.0
Zinc	25.4	10.7	5.5	<5.0	12.6	36.7	5.6	37.6	48.0	20.3

* except for potassium and silicon
** Upper limit of detection
ND = Not Detected

TABLE 7. SUMMARY OF TRACE ELEMENT VALUES IN NETTLE LEAVES FROM SITE 11

Element	Concentration of Trace Element (ppm) in Subsamples									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	6090	806	1860	2960	3020	1601	1460	2140	572	2370
Barium	435	180	250	261	242	244	238	145	288	254
Beryllium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Boron	25.6	40.6	44.0	84.5	41.9	45.4	39.4	38.3	39.6	44.4
Cadmium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Calcium	14800	25000	21900	18800	20100	25500	24200	17800	28700	21900
Chromium										
Cobalt	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Copper	16.9	9.3	15.6	14.5	10.5	10.1	9.7	12.6	12.2	12.4
Iron	3890	309	848	1780	1800	911	657	1490	538	1360
Lead	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Lithium	5.5	5.5	2.9	3.3	3.4	3.0	2.7	3.0	3.6	3.7
Magnesium	8890	3916	5883	6480	6780	9440	8680	6150	7260	7050
Manganese	1060	228	342	808	493	374	554	437	267	507
Molybdenum	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel	9.5	1.9	1.8	8.5	3.6	2.8	2.3	3.0	1.7	3.8
Phosphorus	5340	2220	2400	4240	3650	1650	1500	2180	2000	2800
Potassium	12800	41500	37100	43100	55000	48700	45800	65600	57500	45200
Silicon	78100	2780	6650	20500	21500	6670	4550	5770	3640	16700
Silver	0.2	0.4	0.4	0.5	0.3	0.3	0.4	0.4	0.3	0.3
Sodium	6190	90.8	117	414	334	103	84.4	128	86.3	839
Strontium	104	112	133	90.4	109	167	175	106	148	127.3
Tin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Titanium	1630	48.9	216	613	642	146	99.5	313	91.4	421.8
Vanadium										
Zinc	32.0	43.3	28.1	69.5	26.4	52.2	53.6	32.5	30.0	40.8

ND = Not Detected

TABLE 8. SUMMARY OF TRACE ELEMENT VALUES IN RHODODENDRON LEAVES FROM SITE 11

Element	Concentration of Trace Element (ppm) in Subsamples									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	234	200	212	225	755*	342	331	419	313	337
Barium	186	157	210	198	319	279	270	228	213	229
Beryllium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Boron	25.1	24.6	20.6	27.8	28.2	28.3	29.8	24.8	26.8	26.2
Cadmium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Calcium	14700	14100	13300	14100	18000	18500	15600	12500	15100	15100
Chromium	0.2	0.2	0.2	0.3	1.0	0.7	0.8	0.8	0.8	0.6
Cobalt	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Copper	7.9	5.0	5.2	5.8	7.5	5.3	7.5	67	7.7	6.5
Iron	85.7	83.7	80.4	93.2	367	105	134	186	139	142
Lead	<1.0	<1.0	<1.0	4.9	<1.0	1.8	<1.0	6.6	<1.0	1.5
Lithium	0.4	0.4	0.6	0.5	1.0	0.9	0.9	0.5	1.0	0.7
Magnesium	2260	2410	2020	2330	3730	2930	3310	2230	3000	2690
Manganese	1390	1210	1840	1770	2470	2700	2460	1260	2350	1940
Molybdenum	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel	1.1	<0.5	0.8	2.6	0.7	0.6	1.4	2.3	1.5	1.3
Phosphorus	838	984	920	813	645	699	820	446	674	759
Potassium	14200	12200	9750	5740	10700	8550	11900	8180	13700	10500
Silicon	314	277	239	209	2473*	497	378	576	452	601
Silver	0.7	0.6	0.8	0.9	1.1	1.0	1.0	0.9	1.1	0.9
Sodium	88.3	33.7	59.1	57.5	97.1	23.9	81.7	89.9	91.4	69.1
Strontium	48.2	24.7	30.3	51.7	73.4	64.7	66.2	59.9	56.6	52.8
Tin	0.3	<0.3	0.5	1.1	0.6	0.9	1.1	1.4	1.1	0.8
Titanium	5.3	5.6	4.1	3.5	54.7*	9.3	12.0	16.7	12.8	13.8
Vanadium	2.2	2.1	2.1	2.3	2.6	1.3	1.4	2.0	1.3	1.9
Zinc	18.1	16.1	13.9	13.0	12.6	12.3	12.0	10.9	8.4	13.0

* Possibly contaminated with soil
ND = Not Detected

TABLE 9. SUMMARY OF TRACE ELEMENT VALUES IN FOREST LITTER FROM SITE 12

Element	Concentration of Trace Element (ppm) in Subsamples									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	9983	9057	9643	17167	9863	10336	12066	9740	10600	10940
Barium	277	341	213	285	222	224	229	241	133	241
Beryllium	0.6	1.0	0.7	0.8	0.2	0.4	0.3	1.0	1.2	0.7
Boron	7.6	13.7	8.7	17.4	17.9	16.5	7.3	10.4	12.6	12.5
Cadmium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Calcium	358	1533	163	1.0	207	692	96.0	1054	335	493
Chromium	43.6	49.0	53.0	40.4	29.8	33.7	68.7	38.6	31.0	43.1
Cobalt	1.5	2.6	1.5	3.3	2.1	2.4	4.1	1.7	1.7	2.3
Copper	27.7	24.7	26.6	33.2	18.1	27.1	36.4	36.4	41.1	30.2
Iron	5997	6907	5710	10030	8127	8057	9473	4740	7977	7446
Lead	275	356	259	399	294	308	288	263	290	303
Lithium	6.0	5.8	8.9	17.4	9.0	10.4	12.3	6.9	9.4	9.6
Magnesium	1777	1640	2473	3600	1967	2417	2873	2187	2870	2423
Manganese	598	1180	769	1310	845	1129	1613	224	385	895
Molybdenum	2.6	2.5	2.9	5.4	2.5	2.5	4.2	2.5	3.7	3.2
Nickel	38.5	43.6	45.3	39.4	280	32.8	59.4	33.3	31.8	39.1
Phosphorus	466	3030	1620	560	<50	<50	<50	<50	11100	2036
Potassium	3.33	1.57	5.53	10.55	2.87	1.97	6.50	3.95	4.62	4.53
Silicon	9.8	7.6	10.0*	10.0*	10.0*	9.1	9.8	10.0*	10.0*	9.6
Silver	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sodium	3890	2140	4760	5390	3430	2640	3620	2180	2610	3410
Strontium	30.1	49.7	19.1	19.5	22.8	31.9	15.4	36.7	16.7	26.9
Tin	1.0	2.1	1.7	0.4	1.1	1.7	3.3	0.3	0.1	1.3
Titanium	2000	1281	2130	2453	1643	1467	2343	1199	1603	1791
Vanadium	13.3	13.6	15.4	39.0	18.8	17.1	29.0	8.8	16.8	19.0
Zinc	<5.0	13.1	<5.0	<5.0	15.9	10.9	<5.0	16.5	14.0	7.8

* Upper machine limit
ND = Not Detected

TABLE 10. SUMMARY OF TRACE ELEMENT VALUES IN RHODODENDRON LEAVES FROM SITE 12

Element	Concentration of Trace Element (ppm) in Subsamples									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	251	305	429	196	283	277	447	383	320	321
Barium	336	319	343	359	213	202	317	340	318	305
Beryllium	ND									
Boron	17.8	14.6	12.5	25.6	18.8	19.1	21.0	24.7	21.0	19.4
Cadmium	ND									
Calcium	16700	16300	17200	16200	15000	17200	17500	17900	16900	16800
Chromium	0.4	0.4	0.7	0.2	0.4	0.6	0.6	2.3	0.4	0.7
Cobalt	ND									
Copper	4.5	5.9	5.8	5.8	5.9	6.2	6.0	11.9	5.0	6.3
Iron	75.9	119	188	69.1	80.5	75.2	150	118	92.8	107
Lead	4.5	2.8	2.0	1.8	1.4	<1.0	<1.0	<1.0	<1.0	1.5
Lithium	0.9	1.5	1.5	1.3	1.8	1.7	1.3	1.2	1.4	1.4
Magnesium	2320	2940	3130	2670	2040	2230	2750	2440	2600	2570
Manganese	1440	3230	2710	2060	634	1300	1820	2130	2010	1930
Molybdenum	ND	ND	ND							
Nickel	1.9	1.5	2.0	<0.5	<0.5	<0.5	<0.5	1.1	<0.5	0.9
Phosphorus	498	720	216	1005	861	798	687	746	717	694
Potassium	5400	8910	7950	5160	7850	6170	8100	7660	6210	7050
Silicon	250	355	788	162	296	272	658	591	364	415
Silver	0.9	1.3	1.2	0.8	0.7	0.8	0.8	0.9	0.8	0.9
Sodium	48.2	28.9	50.9	84.0	91.8	79.1	72.1	71.0	52.4	64.3
Strontium	44.7	57.7	52.9	36.8	35.8	36.5	55.3	71.4	66.1	50.8
Tin	0.7	1.4	1.2	1.5	0.5	0.6	0.7	1.3	0.7	1.0
Titanium	8.4	10.2	17.7	8.4	6.8	6.3	22.1	14.2	8.9	11.4
Vanadium	1.5	1.2	1.6	1.2	2.7	2.3	1.8	2.1	1.8	1.8
Zinc	5.5	5.0	<5.0	15.1	13.1	5.7	10.0	9.0	10.1	8.5

ND = Not Detected

TABLE 11. SUMMARY OF TRACE ELEMENT VALUES IN CHRISTMAS FERN FROM SITE 12

Element	Concentration of Trace Element (ppm) in Subsamples									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	786	451	694	683	617	509	784	820	471	646
Barium	86.8	60.9	111	152	117	101	129	88.7	85.8	103
Beryllium	ND									
Boron	10.4	ε.8	12.7	17.6	12.0	9.6	12.4	14.1	6.1	11.5
Cadmium	ND									
Calcium	2850	1620	4960	8650	6450	3490	5290	3360	2070	4300
Chromium	ND									
Cobalt	ND									
Copper	4.1	3.3	7.4	7.2	5.4	4.9	4.9	4.6	4.1	5.1
Iron	174	45	100	126	84.8	57.0	121	79.6	31.2	91.1
Lead	ND									
Lithium	0.6	0.4	0.7	0.9	0.8	0.7	0.8	0.9	0.7	0.7
Magnesium	2430	2790	3050	3010	3380	3010	2580	2700	3230	2780
Manganese	149	172	173	191	169	165	185	199	142	172
Molybdenum	ND									
Nickel	3.4	3.4	3.2	2.9	3.0	3.2	4.2	3.7	3.6	3.1
Phosphorus	304	672	964	980	591	617	569	519	588	645
Potassium	13400	8730	20400	23900	19600	17300	14100	21200	14500	17000
Silicon	702	156	266	416	525	167	679	219	74.2	356
Silver	0.4	0.3	0.4	0.4	0.3	0.3	0.5	0.4	0.4	0.4
Sodium	28.3	<1.0	<1.0	<1.0	<1.0	<1.0	25.9	<1.0	<1.0	6.0
Strontium	34.2	25.0	39.0	51.7	42.8	28.8	44.0	34.7	30.3	36.7
Tin	ND									
Titanium	6.8	0.9	4.5	2.8	9.7	6.1	2.0	8.2	3.7	4.7
Vanadium	ND									
Zinc	11.8	14.6	17.9	22.3	17.8	16.8	9.8	12.9	7.4	14.5

ND = Not Detected

TABLE 12. SUMMARY OF TRACE ELEMENT VALUES IN FOREST LITTER FROM SITE 13

Element	Concentration of Trace Element (ppm) in Subsamples									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	7893	8527	7123	5553	7873	8703	8903	9713	12667	8461
Barium	180	222	208	199	189	262	229	254	332	230
Beryllium	0.8	0.6	0.4	0.3	0.3	0.2	0.2	3.9	5.3	1.3
Boron	15.5	21.0	13.7	31.7	15.9	13.6	5.6	8.9	28.0	17.1
Cadmium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Calcium	851	92	200	232	371	132	151	28	7	229
Chromium	12.3	14.7	15.4	6.1	10.5	13.7	13.5	20.4	29.3	15.1
Cobalt	1.5	1.5	1.5	1.5	1.5	2.4	2.0	1.0	0.5	1.5
Copper	30.8	19.0	18.1	15.9	20.8	22.7	22.3	26.6	25.0	22.3
Iron	6560	5486	4256	3847	6463	7847	5813	6373	8453	6122
Lead	424	459	479	378	453	477	397	610	879	506
Lithium	3.7	4.8	4.5	4.0	5.0	5.0	4.8	3.8	6.1	4.6
Magnesium	1150	1327	1143	934	1277	1647	1813	2130	3413	1648
Manganese	261	200	232	165	274	244	256	227	278	237
Molybdenum	2.0	1.9	1.5	1.1	1.7	2.2	1.8	2.8	3.8	2.1
Nickel	13.1	15.1	15.7	7.3	13.1	14.9	15.4	20.3	29.8	16.1
Phosphorus	1740	1033	226	250	<50	<50	<50	11740	22433	4158
Potassium	0.64	1.18	0.96	0.56	0.55	1.12	1.17	2.45	5.37	1.55
Silicon*	7.3	7.9	7.7	4.4	7.1	6.8	7.5	8.7	10.0	7.5
Silver	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sodium	696	1720	1830	622	1120	1940	2580	3000	5850	2150
Strontium	26.7	21.4	24.5	19.2	22.9	23.3	25.9	14.6	20.8	22.1
Tin	1.2	2.2	2.3	1.6	2.0	2.0	1.1	<0.3	<0.3	1.4
Titanium	857	1400	1073	869	961	1330	1196	1811	2780	1364
Vanadium	11.2	13.7	12.4	11.5	13.4	15.1	14.0	14.8	17.0	13.7
Zinc	52.6	12.4	12.4	17.3	17.9	6.3	9.3	8.2	14.4	16.8

* Upper machine limit
ND = Not Detected

TABLE 13. SUMMARY OF TRACE ELEMENT VALUES IN FOREST LITTER FROM SITE 13

Element	Concentration of Trace Element (ppm) in Subsamples									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	539	766	403	560	466	432	581	572	500	535
Barium	230	181	188	172	169	181	194	222	165	189
Beryllium	ND									
Boron	30.2	24.9	18.6	19.8	19.0	20.0	21.1	21.9	18.2	21.5
Cadmium	ND									
Calcium	14400	5370	5830	7770	5510	5880	4450	6400	6220	6870
Chromium	ND									
Cobalt	ND									
Copper	7.7	7.4	6.4	5.9	6.4	6.4	5.7	6.1	5.3	6.4
Iron	191	293	118	194	180	151	150	139	150	174
Lead	ND									
Lithium	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Magnesium	2730	3520	3760	3550	3430	3320	3450	2770	3490	3340
Manganese	2540	1070	1240	592	1040	1030	312	613	611	1000
Molybdenum	ND									
Nickel	3.6	1.7	2.4	2.8	3.6	3.4	3.2	3.3	4.2	3.4
Phosphorus	1880	1450	978	802	853	945	536	805	563	978
Potassium	7600	27300	22700	26500	19600	26000	17300	19900	19900	20800
Silicon	708	1810	301	494	607	359	2780	1440	690	1020
Silver	0.9	0.3	0.7	0.6	0.7	0.6	0.5	0.6	0.6	0.6
Sodium	86.8	85.1	73.7	72.8	76.7	71.6	75.1	78.2	73.3	77.0
Strontium	56.9	29.5	22.9	27.4	26.1	28.6	31.3	31.0	30.5	31.6
Tin	ND									
Titanium	18.3	22.8	4.4	14.6	12.0	7.8	7.5	7.5	9.9	11.6
Vanadium	ND									
Zinc	46.5	73.8	47.3	44.2	56.3	31.0	39.5	48.8	49.2	48.5

ND = Not Detected

TABLE 14. SUMMARY OF TRACE ELEMENT VALUES IN WITCH HOBBLE FROM SITE 13

Element	Concentration of Trace Element (ppm) in Subsamples									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	598	975	464	613	559	592	655	707	771	659
Barium	242	204	304	286	271	301	258	252	252	263
Beryllium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Boron	28.6	18.1	27.0	27.7	22.5	26.9	23.8	28.8	35.7	26.6
Cadmium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Calcium	13300	5450	16100	15100	13800	14500	11700	12700	14300	13000
Chromium	0.2	<0.2	0.4	0.4	0.5	0.5	0.3	0.2	0.5	0.3
Cobalt	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Copper	6.1	6.5	10.3	9.1	5.8	8.0	8.2	10.0	10.1	8.2
Iron	212	430	164	180	165	229	244	239	298	240
Lead	1.2	<1.0	5.5	7.3	6.7	<1.0	3.7	<1.0	<1.0	2.7
Lithium	1.8	0.7	2.0	1.7	1.3	1.7	1.8	1.9	2.0	1.6
Magnesium	4300	4160	3400	2600	3170	2780	2880	2510	2960	3200
Manganese	1760	635	2560	2490	2280	1710	1770	1910	1640	1860
Molybdenum	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Nickel	<0.5	1.0	<0.5	0.8	<0.5	0.7	0.5	1.4	0.9	0.7
Phosphorus	1220	279	1297	1463	979	1042	878	1323	813	1033
Potassium	4140	24200	8470	10700	6460	3160	8310	12300	15400	10400
Silicon	1440	8110	565	589	596	1140	765	825	1490	1730
Silver	0.8	0.6	1.1	1.1	1.2	0.8	0.9	0.9	0.8	0.9
Sodium	67.1	59.3	86.7	76.5	56.3	76.6	96.5	88.9	81.1	76.5
Strontium	69.3	31.8	64.8	58.8	47.8	73.9	52.7	56.7	77.0	59.2
Tin	1.1	0.3	0.9	0.8	0.4	0.3	0.3	0.3	<0.3	0.5
Titanium	24.3	29.3	16.1	19.5	17.0	20.4	27.6	22.7	34.3	23.5
Vanadium	2.3	2.2	2.3	2.4	2.4	2.5	1.9	2.6	2.2	2.3
Zinc	66.1	56.4	61.2	41.3	33.5	25.9	49.1	31.0	35.0	44.4

ND = Not Detected

TABLE 15. SUMMARY OF TRACE ELEMENT VALUES IN FOREST LITTER FROM SITE 14

Element	Concentration of Trace Element (ppm) in Subsamples									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	8310	15267	5707	5267	10363	8480	6510	11700	4887	8499
Barium	258	272	351	335	211	334	299	282	191	282
Beryllium	2.0	2.0	0.3	<0.2	1.2	0.8	0.2	0.5	0.9	0.9
Boron	12.3	19.2	8.3	6.6	5.4	8.8	5.6	13.7	9.0	9.9
Cadmium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Calcium	750	908	6080	1240	137	515	753	634	3690	1634
Chromium	22.5	16.3	18.8	12.1	20.4	11.5	13.9	31.2	7.9	17.2
Cobalt	3.2	8.2	2.5	4.2	2.2	3.4	3.6	5.1	1.5	3.8
Copper	31.4	54.1	20.1	20.8	29.7	19.2	16.4	40.8	21.7	28.3
Iron	10710	11560	4966	7426	7700	7370	5600	10140	5230	7856
Lead	463	466	106	183	320	353	195	225	119	270
Lithium	10.4	15.3	3.7	3.4	8.2	5.5	3.9	13.1	3.5	7.4
Magnesium	2717	6497	2070	1733	2507	1640	1513	4673	1723	2793
Manganese	1727	4207	1250	1239	1197	932	755	2527	719	1616
Molybdenum	3.2	6.2	1.0	1.1	2.6	1.8	1.4	3.5	0.9	2.4
Nickel	25.6	23.3	20.8	18.5	24.3	17.1	18.6	33.3	17.1	22.1
Phosphorus	1834	1650	1250	<50	1757	953	<50	<50	715	907
Potassium	1.47	3.44	0.34	0.16	2.02	0.85	0.62	2.81	0.27	1.33
Silicon	8.7	9.8	4.9	5.0	10.0*	7.1	4.8	9.7	4.4	7.2
Silver	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Sodium	830	5070	307	421	648	295	216	3450	378	1290
Strontium	21.7	42.5	76.5	57.0	18.1	47.8	41.8	33.5	68.4	45.3
Tin	0.8	<0.3	<0.3	0.8	0.6	1.4	1.4	1.8	<0.3	0.8
Titanium	2457	1263	548	567	1873	1360	850	2017	708	1294
Vanadium	22.1	14.1	6.5	7.6	14.6	12.2	9.1	13.7	4.7	11.6
Zinc	60.8	19.0	17.4	19.0	3.3	29.6	6.5	6.7	42.0	22.7

* Upper machine limit
ND = Not Detected

TABLE 16. SUMMARY OF TRACE ELEMENT VALUES IN RHODODENDRON LEAVES FROM SITE 14

Element	Concentration of Trace Element (ppm) in Subsamples									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	262	284	429	274	334	337	454	464	322	351
Barium	270	243	237	377	260	260	315	272	213	271
Beryllium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Boron	14.4	19.0	16.1	12.7	16.8	20.7	24.5	16.6	15.8	17.4
Cadmium	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Calcium	15200	15800	15600	14800	13500	12100	12900	14700	15200	14400
Chromium	0.3	0.2	0.5	0.4	0.2	0.2	<0.2	0.3	0.2	0.3
Cobalt	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Copper	5.6	5.2	5.5	6.1	6.5	10.9	8.2	5.0	5.9	6.5
Iron	79.3	73.6	131	86.6	116	118	185	154	111	117
Lead	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Lithium	1.4	1.7	1.5	1.6	<0.3	<0.3	<0.3	<0.3	<0.3	0.7
Magnesium	1890	2120	2150	3190	2270	2510	2310	2460	2360	2360
Manganese	963	596	954	1460	1520	2290	2110	707	658	1250
Molybdenum	ND									
Nickel	<0.5	<0.5	<0.5	<0.5	2.1	2.0	2.2	2.3	2.8	1.4
Phosphorus	945	824	883	934	1203	1587	1510	832	965	1075
Potassium	5430	3440	6560	7570	8280	13300	12300	10100	10500	8610
Silicon	300	408	882	384	501	462	711	912	428	554
Silver	0.5	0.5	0.5	0.7	0.6	0.7	0.7	0.5	0.5	0.6
Sodium	22.1	79.0	74.0	23.9	<1.0	<1.0	<1.0	42.8	<1.0	26.9
Strontium	51.8	49.9	78.7	117	93.7	117	141	66.9	61.0	86.4
Tin	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3
Titanium	7.9	8.8	15.2	9.1	10.1	7.2	13.7	12.1	5.6	10.0
Vanadium	1.4	2.0	2.2	2.0	1.3	1.6	1.3	1.2	<1.0	1.5
Zinc	7.0	11.7	11.2	14.4	15.2	22.0	17.4	13.5	15.5	14.2

ND = Not Detected

TABLE 17. SUMMARY OF TRACE ELEMENT VALUES IN YELLOW BIRCH FROM SITE 14

Element	Concentration of Trace Element (ppm) in Subsamples									
	1	2	3	4	5	6	7	8	9	$\bar{X}$
Aluminum	568	274	254	229	178	341	284	203	267	277
Barium	281	422	348	440	295	418	215	207	318	327
Beryllium	ND									
Boron	17.5	19.4	19.0	18.0	24.1	26.5	16.2	17.1	19.0	19.7
Cadmium	ND									
Calcium	16300	17100	15800	16000	14100	25800	16800	10700	17100	16600
Chromium	ND									
Cobalt	ND									
Copper	6.1	8.1	5.2	6.0	6.4	8.2	4.7	6.0	7.4	6.4
Iron	133	115	117	116	101	144	111	117	128	120
Lead	ND									
Lithium	0.7	1.0	0.8	1.4	1.1	1.8	1.1	0.8	1.7	1.1
Magnesium	2510	2290	2170	3760	3170	5670	2960	25000	3500	3170
Manganese	1220	1220	404	1990	1780	2400	808	1750	974	1390
Molybdenum	ND									
Nickel	3.9	4.8	4.1	2.6	3.2	2.5	2.7	4.0	6.4	3.9
Phosphorus	1390	1510	1200	2490	2220	2580	1500	1520	1150	1730
Potassium	12800	41500	37100	43100	55000	48700	13400	9710	20200	18900
Silicon	738	576	637	827	531	2100	833	1660	910	979
Silver	0.9	0.9	0.8	0.9	0.9	1.1	0.5	0.8	0.6	0.8
Sodium	71.1	73.6	71.2	79.2	71.8	751	74.4	75.0	72.8	73.8
Strontium	67.4	93.8	76.5	123	83.9	88.5	55.7	61.8	99.2	83.3
Tin	ND									
Titanium	13.2	13.1	13.7	10.1	7.7	13.1	12.7	7.2	13.0	11.5
Vanadium	ND									
Zinc	32.9	35.7	17.8	105.9	56.7	58.3	65.7	69.3	86.1	58.7

ND = Not Detected

TABLE 18. COEFFICIENTS OF VARIATION FOR ELEMENTAL LEVELS IN VEGETATION SAMPLES COLLECTED IN THE GREAT SMOKY MOUNTAINS BIOSPHERE RESERVE (%)

Sample	Elements				
	Mn	Mg	Al	Sr	Ba
Rhododendron - site 11	21.4	38.5	51.4	30.4	22.3
Rhododendron - site 12	13.5	39.8	25.9	26.0	22.1
Rhododendron - site 14	15.3	50.4	22.3	37.8	17.3
Witch Hobble - site 13	20.5	30.9	22.6	23.9	11.9
Nettle - site 11	27.2	54.2	66.8	28.7	31.1
Christmas Fern - site 12	18.5	10.8	21.9	23.2	26.1
Wood Fern - site 13	10.6	64.6	20.0	34.6	12.1
Yellow Birch - site 14	34.2	45.4	30.9	24.9	26.6

samples in the field and less on reducing or improving analytical precision. Similar types of calculations were made for all elements in the forest litter; however, no deviations from the above pattern were noted.

While this presampling of Great Smoky Mountains National Park was originally designed as a pilot study for a larger project, the results for lead in litter are of particular interest. Levels of lead in soil around power plants range from 5 to 100 ppm (Lindberg et al., 1975; Wiersma and Crockett, 1978). Linzon et al. (1976) reported an overall lead level in soil of 292 ppm in urban areas near a secondary lead smelter. Gill et al. (1974) reported lead levels ranging from 89.3 ppm to 1,403 ppm in soil collected in five U.S. cities. The soil lead levels found in this study were relatively low--15 to 20 ppm--while the lead levels in litter are comparable to lead concentrations found in soil in urban areas.

Sites 11, 12, and 14 are located at relatively low altitudes--near 1,000 m--while site 13 is located at a high altitude--approximately 2,000 m. The lead levels in litter for sites 11, 12, and 14 range between 246 to 303 ppm, whereas the average lead level at the high altitude site, site 13, was 506 ppm. An analysis of variance indicated a significant difference among the four sites at the 99 percent confidence level. An orthogonal comparison confirmed that the lead contamination at site 13 was significantly higher than at sites 11, 12, and 14.

These data are very similar to data reported by Reiners et al. (1975) for the White Mountains of New Hampshire. They reported that lead levels in the litter layer increased with altitude until the Krumholz Forest was reached, where a slight decrease in concentration occurred. The lead levels in the

White Mountains ranged from 35 to 336 ppm, with the fir forest sites having the highest concentrations.

The lead found in the Great Smoky Mountains appears to be from nonnatural sources. Lead levels in soils collected beneath the litter layer are not excessively high. Translocation of lead in vegetation is minimal, and only small amounts of lead were detected in the vegetation sampled. The vegetation samples were collected from the understory. The majority of the litter comes from the overstory canopy (Lutz and Chandler, 1961), which could be an effective filter for airborne lead particles. The air samples did not collect lead; however, the limit of analytical detection was fairly high--50 ng/m^3. Also rain could wash considerable quantities of lead from the air (Schlesinger et al., 1974). Therefore, it is unlikely that the high levels of lead detected in the litter are part of natural lead sources, but rather reflect deposition of lead from outside sources. Similar conclusions were made by Reiners and his research associates (Reiners et al. 1975).

There is some indication that certain plants may be better pollutant accumulators than others. For example, witch hobble is the only understory plant that shows lead residue. Also its average content of elements that may be associated with entrapped dust, such as aluminum and silica, are at least twice as high as those values for rhododendron. This could be related to leaf morphology. Witch hobble has a large broad leaf with a rough surface. Rhododendron leaves are elongated, with a fairly large surface area but a shiny, smooth surface. The results are too preliminary to draw more than an indication of the possible selection of witch hobble as a biological monitor. Other parameters need addressing, such as uptake and translocation, before definite conclusions can be made.

SOIL ANALYSES

Sample preparation included adding 25 ml of concentrated nitric acid to a 10-g aliquot of oven-dried soil. After digestion for a 24-hour period, the soil was separated from the supernatant by centrifugation and filtration and washed three times with distilled deionized water. The supernatant and washes were combined in a volumetric flask and diluted to 100 ml. In addition to the soil extracts, distilled water blanks, acid blanks, standards, and spiked standards were analyzed in duplicate for zinc, lead, copper, cadmium, manganese, and lithium. The analyses were accomplished by standard techniques using a Perkin-Elmer 603 Atomic Absorption Spectrophotometer.

The results are summarized in Table 19. A slight increase in soil lead is present at site 13. The high cadmium level for site 13 is the result of two samples that, when analyzed, gave a high value for cadmium. The quality assurance samples, analyzed simultaneously with the field samples, gave no reason to reject the two high cadmium samples.

TABLE 19. RESULTS OF SOIL ANALYSES FOR GREAT SMOKY MOUNTAINS (µg/g)

	Site 11	Site 12	Site 13	Site 14
Cadmium	1.0	0.9	3.0*	0.8
Copper	5.7**	4.3**	4.3	11.9
Lead	18.0	15.0	20.0	15.0
Lithium	9.8	8.9	4.3	17.7
Manganese	190.2	223.7	39.9	486.9
Zinc	36.0	34.0	21.0	63.0

* Two very high values were detected (14.1 and 9.2 µg/g). When not included, mean cadmium levels for site 13 are 0.5 µg/g.
** Single analysis

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APPENDIX

SCIENTIFIC NAMES OF PLANTS USED IN THIS REPORT

Beech	*Fagus grandifolia*
Black cherry	*Prunus serotina*
Christmas fern	*Polystichum acrosticoides*
Fraser fir	*Abies fraseri*
Hemlock	*Tsuga canadensis*
Magnolia	*Magnolia fraseris*
Nettle	*Laportea canadensis*
Red spruce	*Picea rubens*
Rhododendron	*Rhododendron spp.*
Sugar maple	*Acer saccharum*
Tulip poplar	*Liriodendron tulipifera*
Witch hobble	*Viburnum alnifolium*
Wood fern	*Dryopteris campyloptera*
Yellow birch	*Betula allegheniensis*